Reading Spectral Fingerprints

BY BREEHAN GERLEMAN LUCCHESI

"WHY IS SOLID-STATE NUCLEAR MAGNETIC resonance is so powerful? Because it can tell us how individual atoms are arranged within a material," says Ames Laboratory scientist Marek Pruski. "And, it can tell us how molecules or molecular fragments move in very short time frames."

To obtain this detailed information about materials' structure and dynamics, solid-state NMR monitors the response of atomic nuclei to excitation with radio frequency waves.

"The frequency at which nuclei respond creates a unique spectral 'fingerprint' of their local environment within a material," says Pruski.

These "fingerprints" are especially useful in understanding the structure of non-crystalline materials — that is, materials that do not display regular crystalline structure amenable to diffraction studies. But, solid-state NMR is a challenging business. Because it operates at the low-energy end of the electromagnetic spectrum, the population difference between energy levels involved in NMR transitions is exceedingly small—only a few spins per million effectively generate the NMR signal.

To remedy the sensitivity woes, solid-state NMR experts, like Pruski, are constantly looking for new strategies, which include innovative radio frequency pulse sequences and advanced instrumentation: stronger magnets, state-of-the-art probes, and novel computational tools.

In the last few years, several approaches involving 'hyperpolarization' of nuclear spins have emerged that are poised to revolutionize NMR spectroscopy. Chief among these is dynamic nuclear polarization (DNP). In short, DNP NMR relies upon excitation of the unpaired electrons by microwave irradiation and subsequent transfer of the resulting spin polarization to the material's nuclei, resulting in a much stronger response from these nuclei than is possible in conventional solid-state NMR.

"The frequency at which nuclei respond creates a unique spectral 'fingerprint' of their local environment within a material," **says Pruski.** "These 'fingerprints' are especially useful in understanding the structure of non-crystalline materials—that is, materials that do not display regular crystalline structure amenable to diffraction studies."

In June, Ames Laboratory became home to the first DNP NMR used for materials science in the United States.

"This instrument will allow us to improve the sensitivity by 100 times, and thus take data up to 10,000 times faster," says Pruski.

Commercial DNP NMR systems only became available in the last few years. Pruski and his Ames Laboratory colleague, Takeshi Kobayashi, collaborated with research groups in Europe to demonstrate how useful the DNP NMR will be for materials research at Ames Laboratory.

"We have solid evidence that the DNP NMR is a game-changing technique," says Pruski. "Remarkably, DNP NMR is still emerging. There's great potential for its further development, and we are looking forward to making these advances. Most importantly, however, we want to utilize this new capability within several Ames Lab's research programs to study complex metal hydrides, novel heterogeneous catalysts, biological nanocomposites, thermoelectrics and other energy-related materials."

Serendipity sets Pruski's career path

Ask Marek Pruski what keeps him interested in his work and he doesn't pause for even a second: "Nuclear magnetic resonance is a superbly exciting discipline that continues to develop. And the rate at which it develops just doesn't slow down."

"And, it's just the right mix, for me, of physics and chemistry and experiment and theory. The variety keeps it exciting," he adds.

Pruski's path to joining the solid-state NMR research community was quite serendipitous. He was attending an NMR conference in Poland when he literally bumped into Bernie Gerstein, a former leader of Ames Lab's solid-state NMR program.

"I was coming in a hotel lobby through a revolving door, and Bernie was going out and we ran right into each other. I recognized him as one of the plenary lecturers at the conference, and we got to talking and decided to go to dinner. A three-hour dinner conversation turned into an offer to become a post-doctoral researcher in Bernie's group at Ames Lab."

Pruski joined Ames Laboratory in 1985 as a post-doc and became a staff scientist in 1988. Since then, he's enjoyed being at the leading edge of the field and watching the community of solid-state NMR grow.

"The development of NMR is an absolutely phenomenal thing to watch and be a part of. It's just fascinating. I love it."